PREPARATION AND SULFONATION OF PINANE

A THESIS
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By

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INTRODUCTION

The purpose of this research was to prepare pinane by a method of catalytic hydrogenation heretofore unused, and to check its physical constants against those found in previous researches. In addition, the investigation included a study of the sulfonation of pinane, and the conditions for sulfonation, also a study of the properties of the resulting sulfonic acid. Its properties were considered with a view to the possibility of commercial utilization of the product.

HISTORICAL

Pinane was first reported prepared from l-pinene by Sabatier and Senderens[1] in 1901, using a finely divided nickel catalyst. The vapors of pinene mixed with hydrogen were passed over this catalyst at a temperature of approximately 220°. The boiling point of the original pinene used was not given by Lipp,[3] where this reference was found, and the original reference was not available. The resulting oil was purified and fractionated, giving a liquid which distilled from 165 - 166°. Since that time a number of investigators have prepared pinane by variations of the Sabatier and Senderens process,[2] using nickel, palladium, and platinum catalysts,

(1)Sabatier and Senderens,Comptes Rendues,132,1256,(1901).
(2)(a)Sabatier and Mailhe,Bl.(3),36,615,(1906);(b)Vavon,C.R.149, 98; Bl.(9),9,256;(c)Zelinsky,Ber.44,2784;(d)Nametkin-Jarzeff, Ber.56,832;(e)Nametkin,J.Russ.Phys.Chem.Soc.51,147-51(1920);(f) P. Lipp, Ber.63B, 411-6 (1930).
(3)A. Lipp, Ber. 56B,2098 - 107, (1923).

and reducing with hydrogen in the vapor state. A. Lipp[3] mentions the production of pinane by hydrogenation with a platinum catalyst in the liquid state, first prepared by Fokin and Wilstatter, and prepared later by Lipp, using the Fokin-Wilstatter procedure. For the most part, the variations in physical constants reported may be considered due to experimental error, as the magnitude of these variations is not great. A few of the chemical properties have been investigated and are reported,[2] and also a study of the Raman Spectra.[4]

About the only comprehensive and worth-while review on the subject was published in 1923 by Lipp,[3] who summarized the previous work and did some work himself to verify the structure of pinane. Lipp[3] mentions the pinane produced by various methods which were unpublished, but contained in the theses of the Technische Hochschule, Munich, from 1910 to 1917. Lipp, using pinane prepared by the Sabatier-Senderens process, states that several days action of concentrated sulfuric acid on this pinane caused a rise in the hydrogen and a drop in the carbon values, and a strong decrease in optical activity. He does not attempt to explain this, however, and all other investigators working with supposedly pure pinane report no reaction from sulfuric acid in any concentration.

The freezing point of pinane was reported in Beilstein[5] as -50° for d-pinane prepared from d-α pinene. Freezing point for l-pinane is not given. Lange's Handbook[6] reports -45° for

(4)(a)DuPont,Daure,and Allard, Bull. Soc.Chim.49,1401-9,(1931);
(b)Bonino and Cella,Mem. accad, Italia, chim.2,No.4, 5-51,(1931).
(5)Beilstein,Vol.5, 4th edition supplement, Pg.48.
(6)Lange's Handbook of Chemistry, (1934).

d-pinane. These were subsequently determined during the present investigation to be much too high for the pinane prepared.

EXPERIMENTAL

PINENE

(a) Preparation - 1500 cc gum turpentine, furnished by the U. S. Naval Stores Experiment Station at Olustee, Florida, was distilled in a 45 inch fractionating column. The first 75 cc were rejected, and the subsequent fraction boiling over a range of one degree (155-156° at 737 mm) was retained, put in a bottle containing metallic sodium, and allowed to stand with occasional shaking for a few days. This fraction amounted to approximately 700 cc. This was redistilled in another smaller fractionating column, and the middle portion, boiling over a range of approximately three-fourths of a degree was retained.

(b) Properties - The physical constants determined were boiling range, 155.3 - 156.0° at 738 mm; rotation, -39.4° at 27° C; freezing point -61° to -63°.

The boiling range was measured with a calibrated Anschutz thermometer reading in tenths of a degree. Rotation was measured on an ordinary optical rotation apparatus. The freezing point was measured in a liquid air bath, using a pentane filled thermometer whose error was not more than a degree or two at the temperature of dry ice, and which was correct within error of reading at 0°.

PINANE

(a) Preparation - Pinane was prepared from the pinene previously prepared, by hydrogenation in an Adams type reductor,[7]

(7) Organic Synthesis, Vol. 1, 53, (1932)

using the Raney nickel catalyst[8]. The reductor is a device for shaking and heating a round-bottom flask containing the catalyst and the material to be reduced. A 500 cc round-bottom flask was coated with a 3/16 inch layer of asbestos, around which was wound half of an 18 foot length of No. 30 Chromel wire. Another layer of asbestos was applied, then the rest of the wire wound, after which a final layer of asbestos was put on. The vessel was then air-dried for a few hours, and the drying completed in an oven, then it was wrapped in tire tape. The flask was then clamped in place by its neck on the shaker. The shaker was constructed to give about fifty shakes a minute. A clamped-on stopper for the flask contained a thermometer and a hydrogen intake. Originally, a rubber stopper was used for this, but after two failures gave less than five percent yield, this was given up. Evidently the sulfur in the rubber poisoned the catalyst, for it was ineffective after having been used with the rubber. The final apparatus was equipped with a lead stopper in which the hydrogen intake tube and the thermometer were integrally cast. This was then machined to fit with a shoulder, and a slight circular ridge machined on the shoulder to hold a gasket better. Various materials were tried as a gasket, but cork-filled Neoprene was the best of all used. A coat of Duco paint around the tube and the thermometer reduced hydrogen leakage to practically zero, though it was never quite completely eliminated with the lead stopper. With the lead stopper, the catalyst

(8) Raney, JACS 54, 4116, (1932)

did not seem to decrease in activity, and could be used over and over.

A small intermediate cylinder was used between the large hydrogen cylinder and the flask, to prevent too great pressure on the flask, since a reducing valve was not used. The pressure guage on the intermediate cylinder enabled a closer check on the pressure changes, since the smaller cylinder, which held enough hydrogen at fifty pounds for one run, was shut off from the larger one after being filled. A system of valves was attached to the intermediate cylinder which allowed shutting off either the flask or the large cylinder, or both. Also, the whole system could be evacuated and refilled with hydrogen without changing the connections.

To carry out a hydrogenation, the flask was clamped into place on the shaker. The leads from the resistance wire were connected in series with a lamp bank for temperature control. The flask was heated with 110 volt current. Two hundred cc of pinene and seven to ten grams of catalyst[9] were loaded into the flask, and the stopper clamped on. While the flask was warming up, the air was flushed out by alternately applying suction with a water pump, and then running into the whole system about three atmospheres of hydrogen. For the first run, this was done four times in order to clean out the intermediate cylinder, which had contained air. On subsequent runs, only the flask was flushed out.

(9) The Raney catalyst, after being washed with alcohol and dried in an atmosphere of hydrogen, was kept under pinene in stoppered bottles. Equal weights of pinene and catalyst were present, so that fifteen to twenty gm. of this mixture was used.

Shaking was begun when the temperature reached about 150°. The hydrogen pressure was usually kept at about 45 pounds gage, merely increasing the pressure slightly above 45 every time it dropped to forty or forty-two pounds. On different batches, the temperatures ran from 190 - 210°. The time allowed for hydrogenation, was on various batches from seven to twelve hours.

The resulting liquid was decanted and fractionated once for general use. Following is tabulated a typical result for approximately 140 cc distilled at 738 mm:

14 cc	160 - 164°	water-white
31 cc	164 - 165°	" "
50 cc	165 - 166°	" "
35 cc	166 - 166.5°	" "
10 cc	Residue	yellowish-brown

The three middle fractions are probably practically all pinane, and amount to approximately 80% yield. In addition, half of both end fractions may probably consist of pinane, which if considered will make the yield approximately 90%.

Considering the boiling range of nearly pure pinane as 165.5 to 166.5° at 740 mm, these results for "Boiling range" are just about the average of those previously reported.

(b) Properties - The center fraction of the distillation referred to above is not affected in the cold by permanganate solution, sulfuric acid, or nitric acid, on shaking and allowing to stand for about an hour.

One hundred cc of the pinane boiling over a range of two and a half degrees was fractionated six times in the fraction-

ating column, giving 50 cc of the center fraction that seemed practically constant boiling. This fraction was fractionated once more in a small column. The result of this distillation at 738 mm was as follows:

1 cc	166.2 - 166.6°
3 cc	166.6 - 167.0°
44 cc	167.0 - 167.5°
2 cc	Residue

This 44 cc fraction was utilized for the determination of the physical constants of the pinane. It amounted to about 40% yield on the basis of the original pinene.

The optical rotation, measured at 27° C, was -6.5°.

Its specific gravity, with respect to that of distilled water at 17.5°, was measured with a Westphal balance:

at	17.5°	- 0.8567
	20.0°	- 0.8550
	26.0°	- 0.8509

Its refractive index, measured at 20° with an Abbe refractometer, was 1.4602.

The freezing point determination was made in a large air-jacketed test-tube, immersed in a liquid-air bath in a Dewar flask. A 15 cc sample was used, into which the pentane thermometer was immersed, the pinane being stirred with a loop of copper wire. The average temperature drop was from one to two degrees a minute. The freezing point was based on three determinations: in one the pinane was removed immediately on hardening, in another, it was kept at the semi-hard stage for five minutes, and in the third, it was kept at -80° for ten minutes (just below hardening temperatures), and

then for 45 minutes at the semi-hard stage. Fall and rise of temperature was controlled by changing the depth of immersion in the bath. In all cases, the condition of the pinane seemed to be dependent on the temperature alone, without being affected by the time taken. At no time did the appearance of the pinane change. No crystallization was evident, nor any decrease in clarity, except for a very slight clouding above -40°, which may have been due to a very small amount of water. Water may possibly have been introduced through atmospheric condensation on the wire stirrer, which moved up and down.

At -82° the pinane began to increase in viscosity, becoming more and more syrupy, until at about -100° it was too stiff to continue stirring. This was in contrast to the behaviour of the sample of pinene, which had become definitely crystalline at -62°.

Optical rotation and freezing points were determined (one determination each) on a few other samples selected at random:

Boiling Range at 738 mm	Rotation	Freezing range
160 - 162°		-80 — -120°
163 - 164°	-8.7°	
165 - 166°	-7.5°	-90 — -110°
167½ - 168°		-85 — -105°

SULFONIC ACID FROM PINANE

(a) Preparation

(1) In order to determine whether pinane could be sulfonated with concentrated sulfuric acid, the following experiment was tried: to five cc of pinane were added five cc of 96 - 98% sulfuric acid. This was stirred in a test-tube in an ice-bath for three hours, then allowed to stand. Practically all the original oil separated, and the acid layer was a light orange color. Stirring was continued for three hours at room temperature. About 4½ cc of oil settled out, and the acid layer was brown-colored. Stirring was continued for three hours more at 60°. About 4 cc of oil floated, and the acid layer had become a dark brown. This acid was not extracted.

Since it was evident that only a small amount of sulfonation could be occuring under these conditions, oleum of varying concentrations was used in the subsequent experiments. Two variations of the procedure were used, and are given below:

(2) An amount of pinane, about 5 cc, was put in a test tube and varying amounts and concentrations of oleum were added directly, all at once. The tube was immersed in a bath and stirred for three hours with an air-driven stirrer. At the end of this time, the stirrer was stopped and removed, the pinane unreacted allowed to float. This pinane layer was removed with an elongated medicine dropper and weighed. For the first five runs, the boiling point of the unreacted pinane was checked. However, since it came

out the same as the original each time, or very slightly higher, it was assumed that no reaction had taken place on this oil. (Some of the recovered pinane was sulfonated in three instances, and behaved exactly like the other unused product)

The bottom acid layer was poured slowly on crushed ice, then neutralized with precipitated chalk. This was done because, as with practically all sulfonic acids, the calcium salt is water-soluble. This results in a solution containing a small amount of soluble calcium sulfate and the calcium sulfonic acid salt.

$$2\ RSO_3H + CaCO_3 = Ca(RSO_3)_2 + H_2O + CO_2$$
$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$$

The calcium sulfate was precipitated and filtered off with the excess calcium carbonate. Using this procedure, it was a relatively simple matter to prepare the pure calcium salt of the sulfonic acid. The solution was evaporated to dryness, first by boiling, then the last of the water removed in a vacuum desiccator. The dry salt was taken up with a small amount of water, filtered, and dried again; the process once more repeated, to remove as much as possible of the calcium sulfate.

For analytical purposes, a sample was twice again extracted with water, then the product was submitted to an analysis for Ca and SO_3. Calcium was determined as calcium sulfate by the method given by Scott[10], using 1/20 of all

(10) Scott, Standard Methods of Chemical Analysis, page 107

amounts called for. The salt was dissolved in water and calcium was precipitated in acetic acid solution with ammonium oxalate. The calcium oxalate was filtered off, ignited, then converted to the sulfate with a few drops of conc. sulfuric acid. The sulfate was ignited, weighed, and calculated to calcium.

On basis of $Ca(C_{10}H_{18}SO_3)_2$:

Calcium : Calculated, 0.890% Found, 0.835 ± .02%

SO_3 was determined by digesting 0.1 gm in 100 cc of 20% HCl for three hours at 90 - 95°, then allowing to stand overnight, after which the solution was analyzed for soluble SO_4 by method given by Scott[11].

$$Ca(RSO_3)_2 + HCl = 2\ RSO_3H + CaCl_2$$

$$RSO_3H + HOH = RH + H_2SO_4$$

The small percentage of calcium and the acidity of the solution was such that calcium sulfate did not precipitate. 1/20 of the amounts called for was used. The sulfate was precipitated in hot solution by addition of barium chloride, filtering and weighing in a Gooch crucible.

SO_3 : Calculated, 3.56% Found, 3.6 ± .2%

It was found that if any appreciably greater quantities were used in the digestion with HCl, the results for SO_3 were low. The percentage of hydrolysis became very small when an attempt was made to hydrolyze enough of the sulfonic acid to produce an organic residue of suitable size for identification. Blanks on the HCl used showed no sulfur.

(11) Scott, Standard Methods of Chemical Analysis, page 497

(3) To check on the sulfur dioxide produced in the sulfonation, a few runs were made in a 200 cc four-neck flask, equipped with a mercury-seal stirrer, a separatory funnel for drip-adding oleum or pinane, a thermometer, and an outlet tube. This outlet led through an empty trap into a 500 cc Erlenmeyer containing fifth normal NaOH, which had an outlet to the atmosphere through a soda-lime tube. The round-bottom flask was kept immersed in a bath at the temperature desired.

In general, it was charged with a weighed portion of about 20 cc of pinane, and the acid added through the funnel in half to one hours' time. There was no noticeable rise in temperature, except when the acid was added very rapidly to the pinane while the flask was not immersed in the bath.

The resulting batch was treated in exactly the same manner as in the previous method, after reserving an aliquot portion for the determination of the sulfur dioxide. The sulfur dioxide was determined directly in this solution by titration with tenth normal iodine solution. The soda-lime tubes and caustic were made slightly acid with HCl and titrated with the same iodine solution. Only when the evacuation of the gas was extremely rapid was any sulfur dioxide found in the soda-lime tube, and not much in the caustic.

In an attempt to add 60% oleum into this apparatus, a carbonaceous appearing stalactite formed at the end of the separatory funnel, which eventually clogged the tube, preventing further flow. As a result, only the lower acid concentrations could be used.

The final step in the production of the sulfonic acid was

the addition of the calculated amount of oxalic acid in water solution, to a water solution of the calcium salt. The solution was boiled, filtered and evaporated to dryness. This residue was extracted with a small amount of cold water, filtered, and re-evaporated to produce the free sulfonic acid.

(b) Properties - The free acid is black in color, and gives a dark brown, nearly black, water solution. The dry solid is readily powdered, and quite brittle, but not evidently crystalline. It is soluble in any solution of water, or any liquid containing a reasonable amount of water. With water and practically all solutions it makes a paste with only a few drops. It is also soluble in carbitol, but in no other organic solvents tried, including methyl, ethyl, butyl, and octyl alcohols, acetone, ether, chloroform, carbon tetrachloride, oleic acid, pinene, pinane, ethyl and amyl acetate.

No solvents were found in which it was only partially soluble. Attempts to recrystallize the free acid or the calcium salt by diluting their water or carbitol solutions with organic diluents resulted only in a separation into two liquid layers, one of which contained a very concentrated solution of the sulfonic acid salt.

The free acid is quite hygroscopic, dampening with only a minute's exposure to the air.

It decomposes somewhere above 200 degrees without melting.

Calcium carbonate is not precipitated from a solution of the calcium salt of the acid, on bubbling in CO_2 for an extended period. Calcium oxalate is precipitated when an oxalic acid solution is added to the calcium salt. Evidently the strength, and therefore the ionization constant for the sulfonic acid is somewhere between these two, at approximately $K_1 = 10^{-4}$.

Further work on the properties, and attempts to hydrolyze the acid were done with the calcium salt, and are mentioned under properties of the salts.

SALTS OF SULFONIC ACID FROM PINANE

(a) Preparation

(1) The preparation of the calcium salt is an intermediate step in the production of the acid.

(2,3,4) The sodium, potassium, and ammonium salts were produced in the same manner as the free acid, from the original calcium salt, by double decomposition with the carbonates or oxalates of the corresponding cation. They were also purified in the same manner.

(5) An attempt to prepare the aluminum salt by the same method, using aluminum oxalate prepared in the laboratory, failed. The reason for this is evidently that the salt hydrolyzed, precipitating aluminum hydroxide.

(b) Properties - The salts are non-hygroscopic, or practically so. The calcium salt is dark brown, the sodium, potassium, and ammonium salts a lighter brown. Otherwise there is no evident difference between the properties of

the salts and those of the free acid.

The salts have the same solubilities as the acid, and decompose without melting. The salts are brittle and readily powdered.

An attempt was made to analyze the calcium salt for carbon and hydrogen in a combustion train. After fourteen hours of burning, only 45% of the calculated water and 50% of the calculated carbon dioxide was produced, and the ash was still grey, altho the tube had been heated at approximately 600 degrees.

Ten grams of the calcium salt was heated for two hours at 200° in a sealed tube with 20 cc of water and ten grams of sodium hydroxide. Nothing separated from the solution other than sodium silicate. An ether extraction produced only enough residue to give a faint aromatic odor, which was unrecognizable.

On treatment with fused sodium hydroxide, nothing of any consequence was recovered, and some of the product was decomposed. Any results that might eventually be obtained by pursuing this course more carefully would likely be unreliable, due to instability of terpene structures at the temperature required (310 - 320°). The material was treated in a round-bottom flask fitted with an air reflux having a lead-off tube at the top. A few drops of unidentifiable liquid were recovered, and quantities of a foul-smelling non-condensible gas were evolved.

Heating to about 175° with sulfuric and with phosphoric acids produced no hydrolysis, beyond a small ether extract.

This was merely enough for a faint odor, after three hours heating with the conc. sulfuric acid. Nine grams were dissolved in conc. HCl, and the solution boiled to dryness. The total ether extract amounted to about half a cc and was black and slightly viscous.

Since most salts of sulfonic acids are good wetting agents for cotton it was thought worth-while to try the effect of the calcium salt of this acid. However, a ten percent solution was required to show a wetting effect equal to that shown by some of the products at present on the market, when used in a 0.3 to 0.1% solution.

Eleven grams of the calcium salt was treated with twenty-five grams of phosphorus pentachloride, refluxing for an hour in an oil bath at 150° . The solid mass was extracted with benzene, and the solution poured into conc. ammonia solution. Evaporation of the benzene layer produced about three to five percent yield of a solid soluble in carbitol, amyl acetate, alcohol, and acetone, but insoluble in water and ether. This product was so soluble in alcohol that it could not be recrystallized. Its purification was attempted by succesive solution, filtration, and evaporation, first in alcohol, then in acetone, then in amyl acetate. However, each evaporation resulted in partial decomposition, with a loss of some of the compound. Strangely enough, while the decomposition product was no longer soluble in solvents mentioned, or in water, it would nearly completely dissolve in carbitol, showing that the decomposition was not complete.

This solid also decomposed without melting.

There was about 90% recovery of a water-soluble hygroscopic black powder, which was evidently the original sulfonic acid; also some decomposition into a small residue insoluble in any of the solvents.

RESULTS

A number of runs were made varying the concentration and the amount of acid used. In all but two of these runs, the time of stirring was three hours. One run was stirred for three hours, at the end of which the amount of unreacted pinane was measured, and then replaced for seven hours additional stirring. The pinane was again measured, and the amount was not found to decrease noticeably. Unfortunately, an accident prevented measurement of the final yield of this batch, but all evidence indicated that it was in line with the results of the other runs. Another run was stirred for only 45 minutes. The yield for this run was in agreement with that expected for the same concentration and three hours of stirring. Evidently the time of the reaction is very short, and with highly efficient contact, the process probably could be cut to a few minutes. However, with contact very efficient, efficient cooling would also be necessary. Otherwise the acid would have to be added quite slowly, since a certain amount of heat is liberated.

The results are shown in the following tables, both for runs where sulfur dioxide was measured, and those where it was neglected.

On the graphs, the dots show runs which were made with about 4½ grams of pinane, and ten cc total acid, in an ice bath. Circles indicate the runs made at room temperature, approximately 25°, in a water bath. X's indicate that 20 cc of acid was used, and the runs for these were made in an ice bath. All these runs were made in the test tube. Runs made in the flask are marked with a triangle. These were made in a water bath at room temperature.

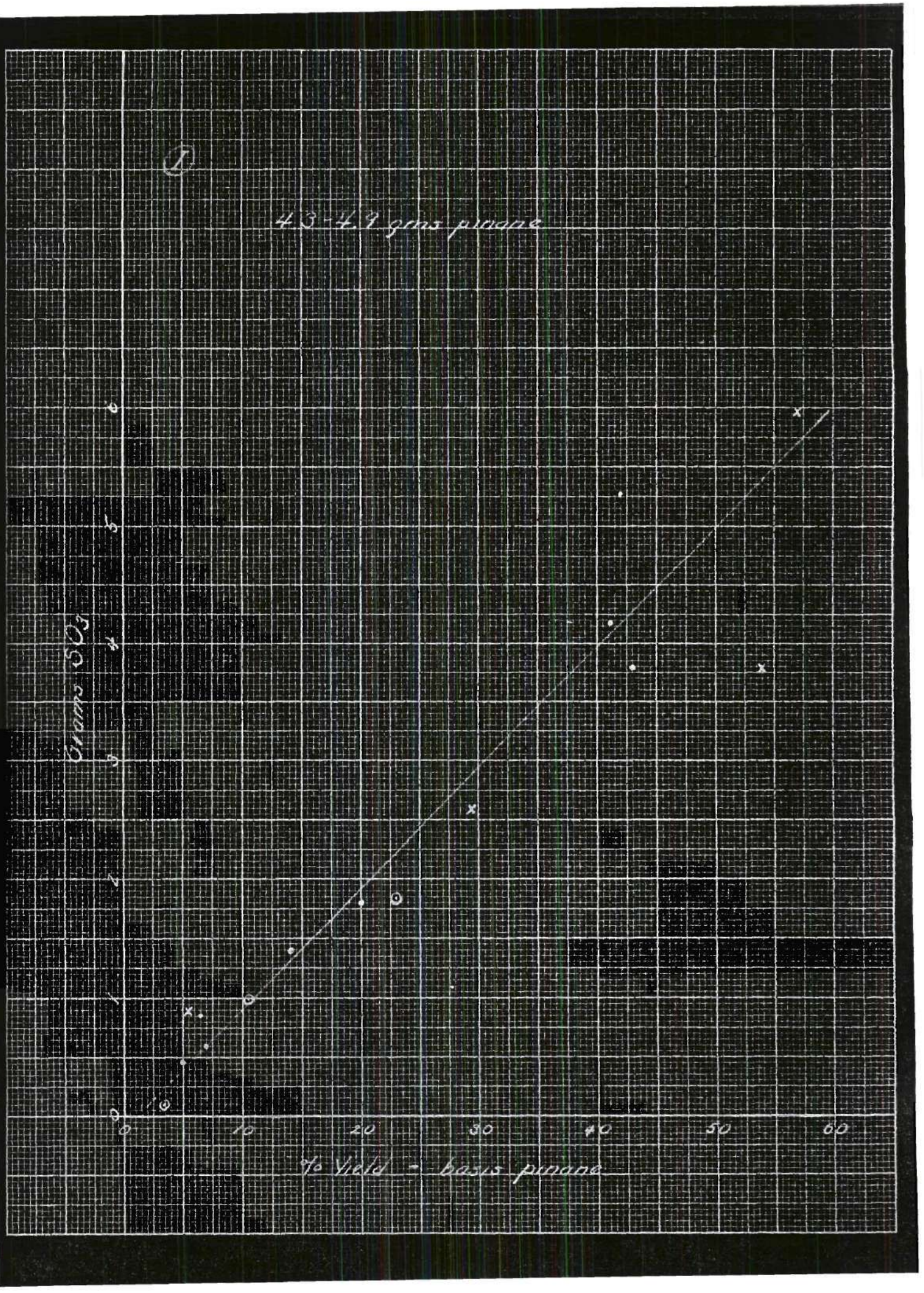
TABLE I

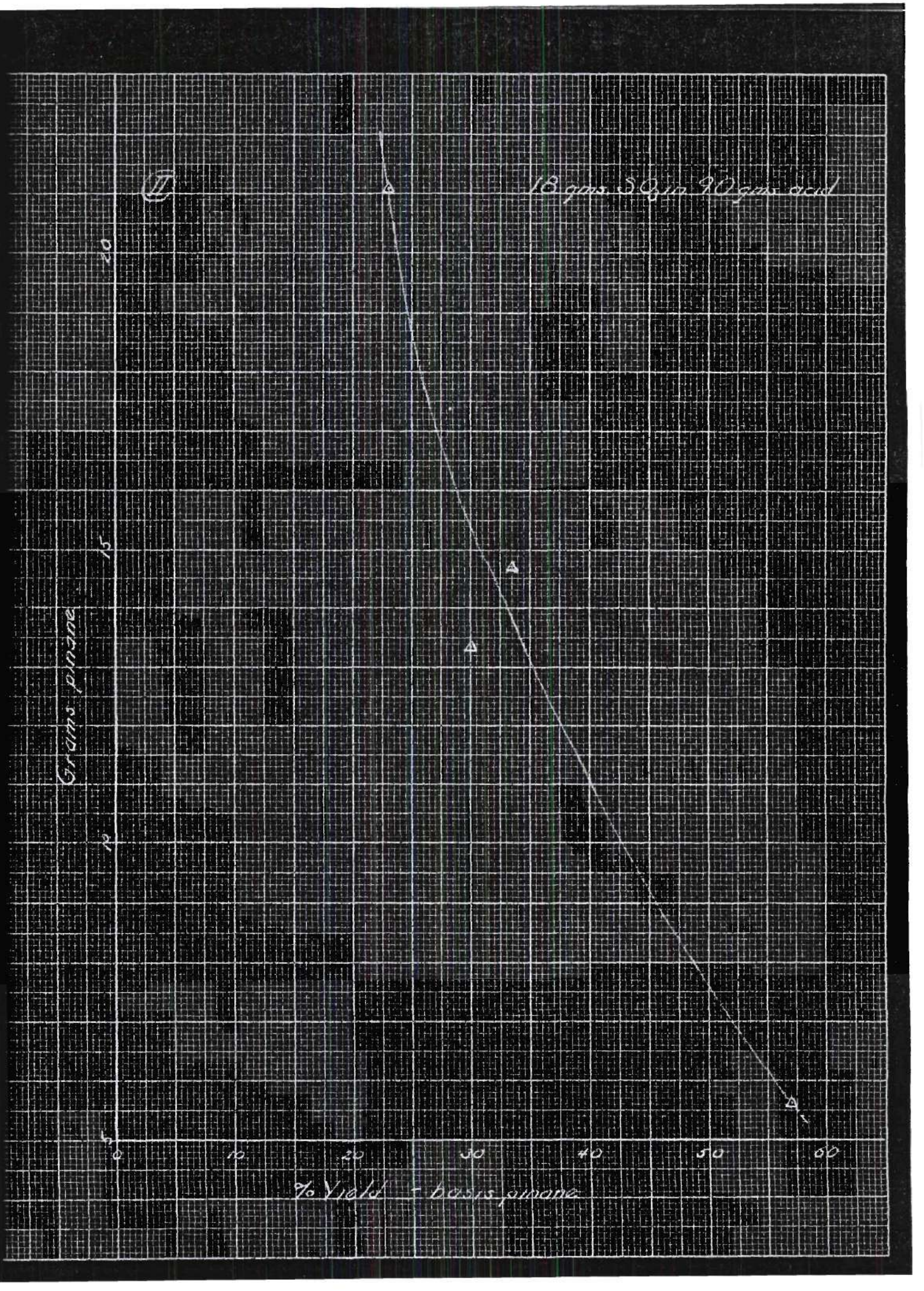
Run No.	Gms. Pinane	Gms. SO_3	% Conc. of Oleum	Total Gms. Acid	% Pinane Recovered	% Sulfonic Acid Salt. Basis: Original Pinane	% Sulfonic Acid Salt. Basis: Free SO_3
1*	4.88	(0.1)	1	8.64	55	3½	(75)
2	4.76	0.45	5	9.06	53	5	(40)
3	4.6	0.6	7	(8.5-9.0)	46	7	35
4	4.27	0.85	10	8.37	50	6½	25
5	4.71	0.9	5	18.0	52	5½	17
6*	4.44	1.0	10	9.97	52	10½	30
7	4.66	1.45	15	9.6	44	14	30
8	4.68	1.80	20	8.94	40	20	35
9*	4.75	1.85	21	9.0	39	23	38
10	4.72	2.6	13	19.77	43	29½	32
11	4.62	3.8	38	10.0	31	43	30
12	4.43	3.8	20	19.03	26	54	38
13	4.75	4.2	42	9.99	40	41	27
14	4.69	5.3	60	8.78	--	42	22
15#	4.69	6.0	33	18.24	38	62	28
16	16.94	27.6	30	91.4	40	42	14
17	17.04	8.15	12½	65.6	41	12½	15
18	21.08	18.6	20	93.0	67	23	15
19	13.34	18.0	20	90.	65	30	13
20	5.63	18.0	20	90.	27	57	10½
21	14.73	18.0	20	90.	54	33½	16
22#	2.80	5.15	60	8.59	29	85	28

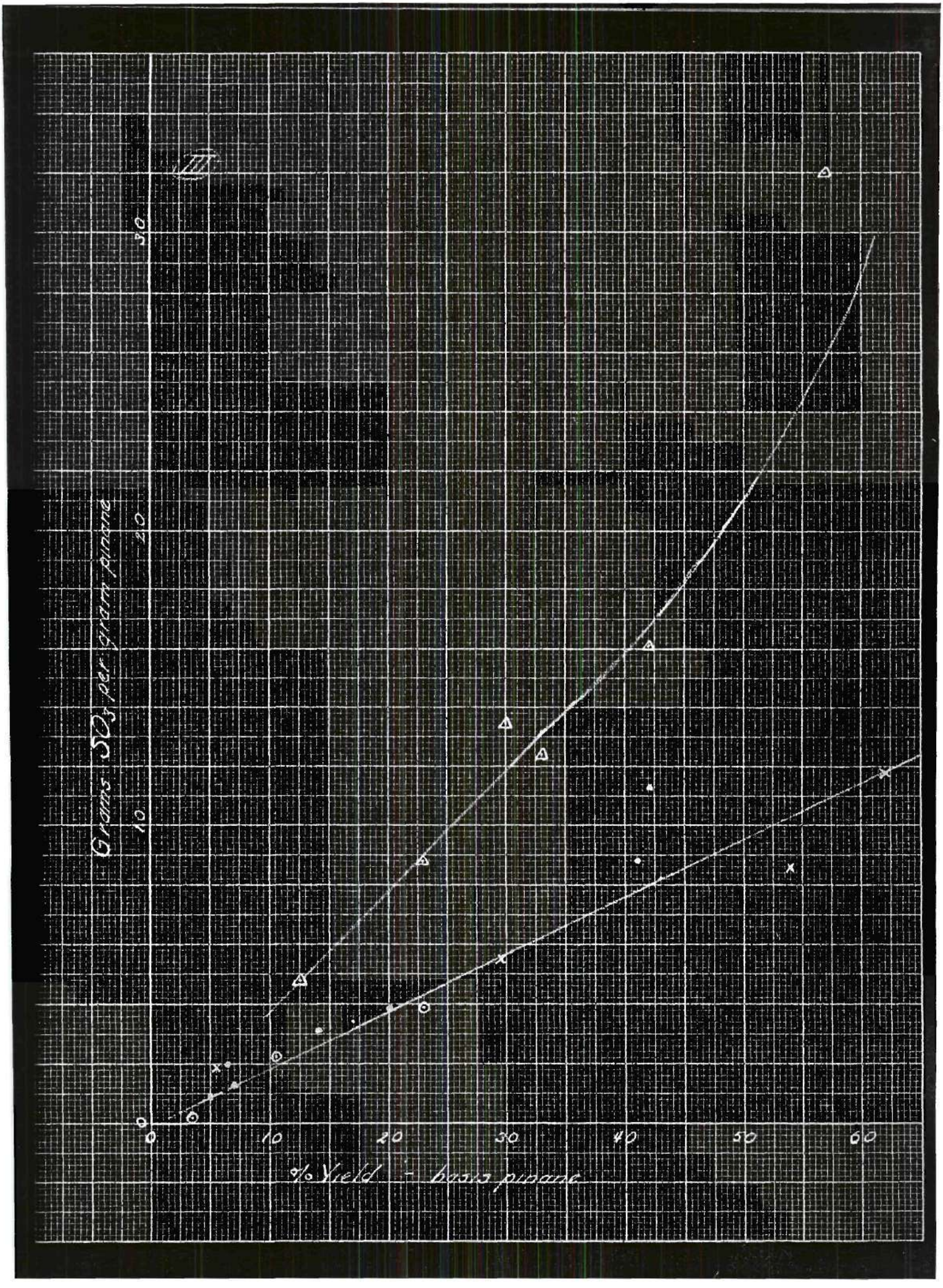
(*)Runs No.1,6,9 and 16 - 22 were made at room temperature -- 25 - 30°.
(#)Runs 15 and 22 show evidence of a possible disulfonic acid (yield is higher than it should be -- 15 gives a 100% total and 22, 114%).
Run No.21 was done in 45 minutes, all others three hours.

TABLE II

Run No.	Mols Pinane Unrecovered	Mols SO_2 Produced	Mols Sulfonic Acid Salt
16	0.0375	0.0441	0.052
18	0.0498	0.0288	0.0350
19	0.0334	0.0225	0.0288
20	0.0298	0.0335(?)	0.0232
21	0.0486	0.0305	0.0360

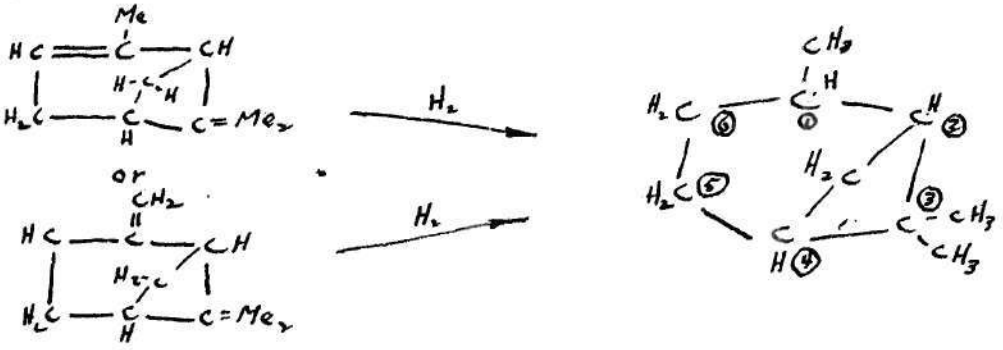

I
4.3-4.9 gms pinane
Grams SO3
0
1
2
3
4
0
10
20
30
40
50
60
% Yield - basis pinane


II
18 gms. SO in 90 gms. acid
20
15
10
5
0
Grams quinine
10.
20
30
40
50
60
% Yield + basis quinine


Grams SO_3 per gram pinane
30
20
10
0
0
10
20
30
40
50
60
% Yield - basis pinane

DISCUSSION

Pinene, besides existing as alpha and beta isomers, has a number of stereo-isomeric forms. When either alpha- or beta-pinene is hydrogenated, a saturated product is formed which has three asymmetric carbon atoms, and therefore possibilities in itself for stereo-isomerism.



If we number the carbons as indicated, we see that numbers 1, 2, and 4 are asymmetric. Since the Me group on 1 may lie on either side of the ring, there may be two isomers due to this carbon. Theoretically, a total of sixteen isomers might exist, since there are three asymmetric carbons. However, if the space formation is considered, it will be seen that only four may exist without undue distortion of the four-membered ring.

Evidently the existence of four stereo-isomers may possibly account for slight discrepancies in results found by different investigators. It may also have something to do with the fact that the mixture produced on hydrogenating pinene boiled over the wide range observed.

It should be particularly taken into consideration at this point that the apparatus used for the most part in investigations reported previous to this one, in particular

for fractionating, was far from efficient. Reports are made on physical properties in many instances, with an indicated error of less than one tenth percent, on a liquid boiling over a two degree range. This is particularly taking much for granted, when it is considered that the three isomers of pinane reported all boil at practically the same temperature. It is practically certain that none of these isomers even approximate 100% purity.

As for the particular fraction chosen for this present work, the only reason that it was taken rather than some other range was the obvious one that this was by far the largest fraction boiling over a half degree range. Yet even with the highly efficient packed column, the final fraction probably is a mixture of isomers, due to the propinquity of their boiling points.

With regard to the freezing points, first of pinene: the discrepancy of approximately twelve degrees found between results of this research and those reported in Lange's handbook and elsewhere, three possible explanations exist. First, the pinene used in this research may have been a mixture of alpha and beta isomers, which are very difficult to separate. Second, the pinene may not have been sufficiently fractionated, although it was twice fractionated in efficient columns, and collected first over one degree, next over three-quarters degree. This would not seem to explain a discrepancy of twelve degrees in the freezing point, however. Thirdly, the earlier results may be in error.

In no references were found results for the freezing point of pinene lower than -55° [12], or of pinane lower than -50°. And though it is true that there is no evidence that the present products are the purest, neither is there any evidence to the contrary. Certainly the discrepancies found are quite out of line with discrepancies which might be expected under ordinary conditions. In particular is this true for the pinane.

The freezing point reported for pinane is for the so-called "d-pinane". Which of the four possible this may be is very doubtful, it is rather almost certain that this refers to a mixture of isomers. No two different sources were found to check each other or this work on the degree of rotation, so that no comparisons can be drawn. It is still safe to say that the present pinane is probably as pure, or purer than any previously reported.

In view of this, the best that can be said of the previous reports of the freezing point of pinane is that they are doubtful, if not actually in error. Although it may be inferred from the difference in rotatory power that the present pinane is a different mixture of isomers from the previous pinanes, the other properties, such as boiling range, specific gravity, refractive index, etc., check as closely as could be desired. Therefore, there is no reason to suspect that the different mixtures of isomers would vary as much as the indicated 40 - 50° in the freezing point.

(12) Beilstein, Vol. 5, fourth edition, page 146

Because of many troubles with leakage in the apparatus used for hydrogenation, a great deal could not be determined with reference to the temperature effect. Also the temperature range did not vary a great deal. Neither could anything be told of the effect of the time, which varied from 7 - 12 hours, for the same reason. In general, the yield seemed practically as good with low temperatures and short periods as with high temperatures and longer periods, as long as the catalyst was functioning.

Probably the temperature could be 50 to 100 degrees lower than the temperatures used. The time required undoubtedly depends on the rate of contact of the catalyst with the hydrogen. Since the reductor was shaken rather slowly, this was necessarily slow. Arrangements could be made to speed this by use of some other apparatus, to get a shorter period.

From an examination of the pinane structure, it will be seen that exclusive of the methyl groups, there are six places where a sulfonic group could be introduced without breaking the rings. Of these, three are tertiary carbon atoms, which are more likely to be attacked by the sulfonating agent than the secondary carbon atoms. Of these, one, the number one carbon is in such a position that the methyl group may cause steric hindrance, and possibly prevent entrance of the sulfonic group at this point, or at least retard it somewhat. This leaves the more probable locations for the sulfonic group, barring molecular rearrangement, in either the 2 or 4 position.

Since all attempts at hydrolysis resulted in decompostion or no reaction, this is a question as yet unanswered. The sulfonic acid investigated may be a mixture of two or even more isomers. Without consideration of steric isomerization there are two or three probable ones, and considering the steric effects, many more may exist. It is even possible that a disulfonic acid may have been formed where large quantities of 60% oleum were used.

Possibly larger quantities of the materials used may have produced more conclusive results, however, from all that could be told in the present work, the sulfonic acid itself is much more stable under treatment than the organic residue would be if it were successfully hydrolyzed off.

In this respect, the present sulfonic acid is different from that of benzene, which is readily hydrolyzed with both alkali and acids. Also, the sulfonamide of benzene is readily prepared with PCl_5, whereas only a small amount of alcohol and benzene soluble residue was obtained with the present sulfonic acid. This decomposed without melting, while the sulfonamide of benzene is readily recrystallized and has a definite melting point.

Its solubility, however, is in line with that of practically all other sulfonic acids, in particular since the salts of the heavy metals are readily water-soluble.

From the sulfonation a certain amount of by-product --- averaging about twenty-five percent --- was recovered by ether-extraction of the calcium carbonates and sulfates filtered from the solution. This was evidently a mixture

of polymerized and decomposed hydrocarbons. It was viscous, sticky, and dark brown. Half of it distilled between 165 and 250° (at 10 mm), with no definite fraction anywhere evident. The residue changed in appearance only in that it became nearly solid, and very much more sticky. It was not further investigated, other than noting that on standing it increased in viscosity, probably through air oxidation. After a few weeks, some left on a watch-glass had become solid and somewhat brittle.

It was noted in some of the later runs, that the products produced were hygroscopic, and on analyzing these for Ca, the results were found to be as much as 50 - 60% low. This percentage of Ca could be increased by boiling the acid with lime.

The reason for this result may be found in the fact that the later runs were made with more speed than the earlier runs, so that the acid may not have had time to be neutralized.

The results in the test-tube sulfonation and those in the flask were for the most part comparable, although the yield from the test-tube sulfonation was in general slightly higher. This seemed natural enough in view of the fact that there was more agitation in the test tube than in the flask, where the small amount of material spun much more than it mixed. The change of thirty degrees from an ice-bath to room temperature seemed to have only a negligible effect on the results. The primary consideration in the sulfonating was good contact of the reactants, thorough agitation, since the difference in specific gravities is great.

In general the accuracy of the measurements made was greater than the reproducibility of results.

In consideration of the three curves included: First, curve number one (I) of Grams SO_3 against yield on the basis of pinane. Here only two points are definitely off the curve. Neither of these can be explained by the change in concentration. In the case of the point which gives a higher yield than the curve indicates (see Table I, run 12), the concentration is about half that of the run (number 11) nearest it with the same weight of SO_3. The difference is found in that run 12 contains about twice the amount of hydrogen sulfate. Again, in the case of the point giving the lower yield, (run 14), it is seen that while the concentration of oleum for this run is almost twice that of the next run (number 15), the lower yield may be explained by the fact that there is much less hydrogen sulfate.

It is seen that the runs at room temperature fall in line with those done at ice bath temperature.

From this curve, we may conclude that if the amount of pinane is kept constant, the yield increases almost in proportion to the weight of sulfur trioxide. Also, that increased amounts of hydrogen sulfate, (decreased concentration) also tend to give higher yields. Possibly some water may be formed which is removed by the hydrogen sulfate.

Four runs (18 - 21) are shown on curve number two (II) of Grams pinane against yield on the basis of pinane. In these runs the acid was kept constant. These indicate that the

percent yield based on pinane decreases, as the amount of original pinane increases. At the same time, there is a small increase in the amount of salt produced, showing that the amount of pinane has some effect, though not nearly as strong as the effect of increasing SO_3.

Another graph is shown, curve number three (III), in which the Grams SO_3 per gram pinane is plotted against the percent yield, based on pinane. The curve for the runs in the flask is different from the curves for the run in the test tube -- possibly lack of efficient contact in mixing is the cause. In general, both curves show the same tendencies previously mentioned, i.e., increase in yield with increase in SO_3, with only a slight concentration effect.

It should be of interest to make a series of runs keeping the SO_3-pinane ratio constant and varying the amount of hydrogen sulfate.

The lack of wetting power of this sulfonic acid in comparison with other sulfonic acids may be ascribed to the dissimilarity between the terpene end of the molecule and the cotton fats, in which the terpene end must dissolve to wet the cotton. Either it is not sufficiently soluble in the cotton fats, or else it is so short that the excessive polarity of the compound will not allow sufficient surface action to come into play. As a matter of fact, the more efficient wetting agents contain from 15 to 20 or more carbon atoms, and most of them are straight-chain compounds.

Not much could be told about the results with the sulfur dioxide. It can be seen from Table II that the sulfur dioxide formed was almost equivalent to either the pinane decomposed or the sulfonic acid salt formed. More probably it was connected with the decomposition of the pinane, through oxidizing pinane even at the low temperatures which were used in the experiments. As this is probably the case, no conclusions may readily be drawn, since the amount of sulfur trioxide reduced to the dioxide for a certain amount of pinane is not at all definite. There is no reason to suppose that the pinane was oxidized before the formation of the sulfonic acid, since such a postulation would infer subsequent oxidation. The process of sulfonation itself is neither oxidation nor reduction.

SUMMARY

Pinene from gum turpentine was hydrogenated by a new procedure using a Ni catalyst to produce pinane. The properties of the resulting pinane were checked and the freezing point of pinane redetermined (about -90°). A sulfonic acid and a few of its salts were produced from the pinane, using oleum as the sulfonating agent. A study of the conditions of sulfonation, including amounts and concentrations of oleum compared to yield, was made. The properties of the free acid and its salts were investigated.